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(71) Applicant: Halliburton Energy Services, Inc.  
Duncan, Oklahoma 73536 (US)

(72) Inventors:

- Nguyen, Phillip D.  
Duncan, Oklahoma 73533 (US)
- Barton, Johnny A.  
Marlow, Oklahoma 73055 (US)

(74) Representative: Wain, Christopher Paul et al  
A.A. Thornton & Co.  
235 High Holborn  
London WC1V 7LE (GB)

### (54) Resin-coated proppant for subterranean fractures

(57) Resin-coated proppant particles are suspended in a fracturing fluid and deposited in a subterranean fracture and consolidated into high strength permeable masses. As the fractures are formed, a liquid hardenable resin component is continuously mixed with a liquid hardening agent component on-the-fly to form a hardenable resin composition. The hardenable resin compo-

sition is continuously coated onto dry proppant particles on-the-fly to form resin composition coated proppant particles, and the resin composition coated proppant particles are continuously suspended in the fracturing fluid on-the-fly.

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**Description**

[0001] The present invention relates to a method of providing resin-coated proppant in a subterranean fracture.

[0002] Hydrocarbon producing wells are often stimulated by hydraulic fracturing treatments. In hydraulic fracturing treatments, a viscous fracturing fluid which also functions as a carrier fluid is pumped into a producing zone to be fractured at a rate and pressure such that one or more fractures are formed in the zone. Particulate solids, e.g., graded sand, for propping the fractures, commonly referred to in the art as "proppant" are suspended in a portion of the fracturing fluid so that the particulate solids are deposited in the fractures when the fracturing fluid is broken. That is, a breaker is included in the fracturing fluid whereby the fracturing fluid reverts to a thin fluid which is returned to the surface. The proppant deposited in the fractures functions to prevent the fractures from closing so that conductive channels are formed through which produced hydrocarbons can readily flow.

[0003] In order to prevent the subsequent flow-back of proppant as well as loose or incompetent sand in the fractured zone with fluids produced therefrom, a portion of the proppant introduced into the fractures has heretofore been coated with a hardenable resin composition which is caused to harden and consolidate the proppant particles in the zone.

15 Typically, the resin composition coated proppant is deposited in the fractures after a large quantity of uncoated proppant has been deposited therein. That is, the last portion of the proppant deposited in each fracture, referred to in the art as the "tail-end" portion, is coated with the hardenable resin composition. When the viscous fracturing fluid which is the carrier fluid for the proppant is broken and reverts to a thin fluid as described above, the resin coated proppant is deposited in the fractures and the fractures close on the proppant. The partially closed fractures apply pressure on the 20 resin coated proppant particles whereby the particles are forced into contact with each other while the resin composition hardens. It has heretofore been thought that the hardening of the resin composition under pressure brings about the consolidation of the resin coated proppant particles into a hard permeable pack having sufficient compressive and tensile strengths to prevent unconsolidated proppant and formation sand from flowing out of the fractures with produced fluids. However, it has been found that as the fracturing fluid containing proppant without a hardenable resin composition 25 coating thereon is carried into the fractures by the fracturing fluid, some of the proppant is continuously deposited in the bottom of the fractures adjacent to the well bore. This unconsolidated accumulation of non-resin coated proppant remains in the fractures adjacent to the well bore and when the resin coated proppant enters the fractures at the end of the proppant deposit, it does not displace the uncoated proppant at the bottom of the fractures. Instead, the resin coated proppant flows over the uncoated proppant. This results in unconsolidated proppant at the bottom of the fractures adjacent to the well bore. During the subsequent production of formation fluids through the propped fractures, 30 the unconsolidated proppant at the bottom of the fractures flows back with the formation fluids. The flow-back of the proppant with the formation fluids is very detrimental in that it erodes metal goods, plugs piping and vessels and causes damage to valves, instruments and other production equipment.

[0004] Thus, there are needs for improved methods of consolidating proppant particles in subterranean fractures 35 whereby all of the proppant particles are consolidated into high strength permeable packs in the fractures which do not permit the flow-back of proppant, formation sand and the like.

[0005] In one aspect, the present invention provides a method of providing resin-coated proppant particles in a fracture in a subterranean zone, which method comprises

40 (a) pumping gelled liquid fracturing fluid into said subterranean zone to form one or more fractures therein, and;  
 (b) as said fractures are formed in step (a), continuously mixing a liquid hardenable resin component with a liquid hardening agent component on-the-fly to form a hardenable resin composition; said liquid hardenable resin component being comprised of a hardenable resin, a silane coupling agent, a solvent for said resin, one or more hydrolysable esters for breaking gelled fracturing fluid films on proppant particles, and a surfactant for facilitating 45 the coating of resin on said proppant particles and for causing said hardenable resin to flow to the contact points between adjacent resin coated proppant particles; and said liquid hardening agent component being comprised of a hardening agent suspended or dissolved in a liquid carrier fluid;  
 (c) continuously coating said hardenable resin composition produced in step (b) onto dry proppant particles on-the-fly to form resin composition coated proppant particles;  
 50 (d) continuously mixing said resin composition coated proppant particles produced in step (c) with said fracturing fluid pumped in accordance with step (a) on-the-fly whereby said resin composition coated proppant particles are suspended therein;  
 (e) terminating steps (a), (b), (c) and (d) when said resin composition coated proppant particles have been placed in said one or more fractures; and  
 55 (f) allowing said hardenable resin composition on said resin composition coated proppant particles to harden and consolidate said proppant particles into one or more high strength permeable packs which prevent proppant particle flow-back.

[0006] The present invention provides improved methods of coating dry proppant particles with a resin composition and suspending the coated proppant particles in a fracturing fluid. The resin composition hardens and consolidates the resin coated proppant particles into high strength permeable packs in fractures formed in subterranean zones which do not allow proppant flow-back. The methods are basically comprised of the following steps. A liquid hardenable resin component is provided comprised of a hardenable resin, a silane coupling agent, a solvent for the resin, a hydrolyzable ester for breaking gelled fracturing fluid films on the proppant particles, and a surfactant facilitating the coating of the resin on the proppant particles and for causing the hardenable resin to flow to the contact points between adjacent resin coated proppant particles so that the particles are consolidated into a high strength permeable mass. A liquid hardening agent component is provided comprised of a hardening agent suspended or dissolved in a liquid carrier fluid. In addition, a source of dry proppant particles and a gelled liquid fracturing fluid are provided. The gelled liquid fracturing fluid is pumped into a subterranean zone to form one or more fractures therein and to place resin composition coated proppant particles in the fractures. As the fractures are formed by the fracturing fluid, the liquid hardenable resin component is mixed with the liquid hardening agent component to form a resin composition. The resin composition is continuously coated on dry proppant particles conveyed from the source of the dry proppant particles. The resulting resin composition coated proppant particles are continuously mixed with the fracturing fluid whereby the resin composition coated proppant particles are suspended in the fracturing fluid and are deposited in the one or more fractures formed wherein they are caused to harden and consolidate into a high strength permeable pack which prevents proppant flow-back. When the resin composition coated proppant particles have been placed in the one or more fractures, the pumping of the fracturing fluid, the mixing of the liquid hardenable resin component with the liquid hardening agent component, the coating of the dry proppant particles with the resin composition and the mixing of the resin composition coated proppant particles with the fracturing fluid are terminated. The hardenable resin composition on the coated proppant particles is allowed to harden and to consolidate the proppant into one or more high strength permeable packs which prevent proppant flow-back.

[0007] Another improved method of the present invention for coating dry proppant particles with a resin composition and suspending the coated proppant particles in a fracturing fluid whereby the resin coated proppant particles are placed in one or more fractures formed in a subterranean zone by the fracturing fluid is comprised of the following steps. A liquid hardenable resin component as described above and a liquid hardening agent component as described above are provided along with a source of dry proppant particles and a gelled liquid fracturing fluid. The gelled liquid fracturing fluid is pumped into the subterranean zone to form one or more fractures therein and to place the resin composition coated proppant particles in the fractures. The liquid hardenable resin component is continuously mixed with the liquid hardening agent component to form a resin composition. The volume ratio of the liquid hardening agent component to the liquid hardenable resin component is varied from an initial volume ratio to a lower volume ratio and then back to the initial volume ratio in order to consolidate all of the proppant particles in the fractures while conserving the amount of the liquid hardening agent component used. The resin composition is continuously coated onto dry proppant particles conveyed from the source thereof to form resin composition coated proppant particles. The resin composition coated proppant particles are continuously mixed with the fracturing fluid so that the resin composition coated proppant particles are continuously deposited in the fractures. Thereafter, the pumping of the fracturing fluid into the subterranean zone, the mixing of the liquid hardenable resin component with the liquid hardening agent component, the coating of the resin composition onto the dry proppant particles to form resin composition coated proppant particles and the mixing of the resin composition coated proppant particles with the fracturing fluid are terminated. The hardenable resin composition on the coated proppant particles is allowed to harden and to consolidate the proppant into one or more high strength permeable packs which prevent proppant flow-back.

[0008] As mentioned above, the prior art methods of consolidating proppant in subterranean fractures have generally included the placement of a large quantity of uncoated proppant in the fractures followed by a tail-end portion of proppant coated with a hardenable resin composition. When the viscous fracturing fluid which is the carrier for the proppant is broken and reverts to a thin fluid, the resin coated proppant is deposited in the fractures. The tail-end portion of the resin coated proppant is consolidated into a hard permeable mass by the resin composition, but the uncoated proppant previously deposited in the bottom of the fractures as the large quantity of uncoated proppant was transported into the fractures is not consolidated. As a result, when the well is placed on production, flow-back of the uncoated proppant takes place.

[0009] Another problem which is encountered in consolidating the proppant to prevent flow-back involves the strength of the consolidated resin coated proppant packs in the fractures. Heretofore, it has been a common practice to utilize proppant that is precoated with a resin composition and stored. When the precoated proppant is required for use at a job site, it is transported to the job site. While such precoated resin coated proppant is consolidated after being placed by a hardening agent, the resulting consolidated proppant pack often does not have enough strength to prevent deterioration and proppant flow-back.

[0010] In accordance with the present invention, all of the proppant transported into the fractures is coated with a resin composition on-the-fly as the fracturing fluid is pumped into the well bore and into the fractures. As a result, the

resin coating on the proppant is fresh and when it hardens and consolidates the proppant, high strength permeable proppant packs are formed in the fractures which prevent proppant flow-back. As will be described further hereinbelow, in order to conserve the amount of hardening agent utilized for curing the hardenable resin which has been deposited on all of the proppant in the fractures, the volume ratio of liquid hardening agent component to liquid hardenable resin component utilized in accordance with this invention is varied. In a preferred technique, the volume ratio of the liquid hardening agent component to the liquid hardenable resin component is varied from an initial volume ratio at the beginning of the proppant suspended in the fracturing fluid to a lower volume ratio as the middle portion of the proppant is suspended in the fracturing fluid and then back to the initial volume ratio at the end portion of the proppant suspended in the fracturing fluid. This technique results in consolidated proppant packs in the fractures which have high strength at the forward ends of the packs, less strength at the middle portions of the packs and high strength at the end portions of the packs. The middle portions of the packs tend to be placed deeply in the fractures far away from the well bore. Since all of the proppant is consolidated, there is no unconsolidated proppant remaining in the bottoms of the fractures and as a result proppant flow-back does not occur.

[0011] In accordance with the improved methods of this invention, dry proppant particles are coated with a resin composition on-the-fly, the coated proppant particles are suspended in the fracturing fluid on-the-fly and the resulting hardenable resin composition coated proppant particles are placed in one or more fractures formed in a subterranean zone. Such methods are basically comprised of the following steps. A liquid hardenable resin component is provided comprised of a hardenable resin, a silane coupling agent, a solvent for the resin, a hydrolyzable ester for breaking gelled fracturing fluid films on the proppant particles, and a surfactant for facilitating the coating of the resin on the proppant particles and causing the hardenable resin to flow to the contact points between adjacent resin coated proppant particles so that the particles are consolidated into a high strength permeable mass. A liquid hardening agent component is provided comprised of a hardening agent suspended or dissolved in a liquid carrier fluid. In addition, dry proppant particles and a gelled liquid fracturing fluid are provided. The gelled liquid fracturing fluid is continuously pumped into a subterranean zone to form one or more fractures therein and to place the resin composition coated proppant particles in the fractures. As the fractures are formed by the fracturing fluid, the liquid hardenable resin component is continuously mixed with the liquid hardening agent component on-the-fly to form the resin composition. The resin composition is continuously coated on the dry proppant particles which are conveyed from the source thereof on-the-fly to form resin composition coated proppant particles. The resin composition coated proppant particles are continuously mixed with the fracturing fluid on-the-fly whereby the resin composition coated proppant particles are suspended therein. Thereafter, the resin composition coated proppant particles are carried into the fractures whereupon the pumping of the fracturing fluid and other related steps are terminated. As is well understood by those skilled in the art, the gelled liquid fracturing fluid can include a breaker which causes it to revert to a thin fluid so that the resin composition coated proppant particles are deposited in the fractures and the fracturing fluid is returned to the surface.

[0012] The term "on-the-fly" is used herein to mean that a flowing stream is continuously introduced into another flowing stream so that the streams are combined and mixed while continuing to flow as a single stream. As is also well understood, when the fracturing fluid is broken and the resin composition coated proppant particles are deposited in the fractures formed, the fractures close on the proppant particles. The partially closed fractures apply pressure on the resin composition coated proppant whereby the proppant particles are forced into contact with each other while the resin composition hardens. The hardening of the resin composition under pressure helps bring about the consolidation of the resin coated particles into a hard permeable pack having sufficient compressive strength to prevent unconsolidated proppant and formation sand from flowing out of the fractures with produced fluids. As is also understood, in fracture treatments carried out in unconsolidated formations, good consolidation of proppant is required in the perforations which extend from the inside of the well bore through casing and cement into the unconsolidated formation as well as in the fractured portions of the unconsolidated formation surrounding the well bore. The tail-end portion of the proppant which is deposited in the perforations and in the fractures is coated with a hardenable resin composition and is caused to harden. The resulting consolidated proppant in the perforations and fractures contributes to the prevention of proppant flow-back. However, there is often little closure pressure applied to the resin coated proppant in the fractures close to the well bore and there is no closure pressure applied to the resin coated proppant particles in the perforations. In addition, the resin coated proppant particles can be separated from each other by films of the gelled fracturing fluid and because of the presence of the fracturing fluid films, the proppant particles do not sufficiently consolidate. As a result, the consolidated permeable packs formed in the perforations and fractures often have less than sufficient compressive strength to prevent unconsolidated proppant and formation sand from flowing out of the perforations and fractures. These problems are solved by including one or more hydrolyzable esters which function to break gelled fracturing fluid films on the particles, and a surfactant for facilitating the coating of the resin composition on the proppant particles and for causing the hardenable resin to flow to the contact points between adjacent resin coated proppant particles so that the particles are consolidated into a high strength permeable mass.

[0013] As mentioned above, in accordance with the present invention all of the proppant particles are coated with the liquid hardenable resin composition. In order to conserve the liquid hardening agent component used and to reduce

the cost of the fracturing procedure, the volume ratio of the liquid hardening agent component can be varied. That is, in a preferred technique, the volume ratio of the liquid hardening agent component to the liquid hardenable resin component is varied from an initial volume ratio which produces a high strength permeable pack to a lower volume ratio which produces a lower strength resilient permeable pack and then back to the initial volume ratio which produces a high strength permeable pack adjacent to the well bore. As mentioned, because all of the proppant particles are coated with the liquid hardening agent component, there is no unconsolidated proppant particles in the bottoms of the fracture and consequently, the consolidated permeable pack does not allow flow-back to occur. The initial volume ratio of the liquid hardening agent component to the liquid hardenable resin component is generally in the range of from about 1:100 to about 1:2 and the lower volume ratio is in the range of from 0 to about 1:5. Preferably, the initial volume ratio of the liquid hardening agent component to the liquid hardenable resin component is about 1:2 and the lower volume ratio is about 1:10.

[0014] Thus, another method of the present invention includes the following steps. A liquid hardenable resin component is provided comprised of a hardenable resin, a silane coupling agent, a solvent for the resin, one or more hydrolyzable esters for breaking gelled fracturing fluid films on the proppant particles, and a surfactant for facilitating the coating of the resin on the proppant particles and for causing the hardenable resin to flow to the contact points between adjacent resin coated proppant particles. A liquid hardening agent component is provided comprised of a hardening agent suspended or dissolved in a liquid carrier fluid. In addition, a source of dry proppant particles and a gelled liquid fracturing fluid are provided. The gelled liquid fracturing fluid is pumped into the subterranean zone to form one or more fractures therein and to place the resin composition coated proppant particles in the fractures. As the fractures are formed the liquid hardenable resin component is continuously mixed with the liquid hardening agent component on-the-fly to form the resin composition. The volume ratio of the liquid hardening agent component to the liquid hardenable resin component is varied, and the resin composition produced is continuously coated onto dry proppant particles conveyed from the source thereof on-the-fly to form resin composition coated proppant particles. The resin composition coated proppant particles are continuously mixed with the fracturing fluid being pumped on-the-fly whereby the resin composition coated proppant particles are suspended therein. After the resin composition coated proppant particles have been placed in one or more fractures formed in the subterranean zone, the pumping of the gelled liquid fracturing fluid and other related steps are terminated. Thereafter, the gelled liquid fracturing fluid breaks into a thin fluid, the resin composition coated proppant particles are deposited in the fractures and the resin composition hardens and consolidates the proppant particles in one or more fractures into high strength permeable packs which do not allow proppant flow-back.

[0015] Examples of hardenable resins which can be utilized in the liquid hardenable resin component include, but are not limited to, organic resins such as bisphenol A-epichlorohydrin resin, polyepoxide resin, novolak resin, polyester resin, phenol-aldehyde resin, urea-aldehyde resin, furan resin, urethane resin and mixtures thereof. Of these, bisphenol A-epichlorohydrin resin is preferred. The organic resin utilized is included in the liquid hardenable resin component in an amount in the range of from about 50% to about 90% by weight of the liquid hardenable resin component, preferably an amount of about 85%.

[0016] Examples of silane coupling agents which can be used include, but are not limited to, N-2-(aminoethyl)-3-aminopropyltrimethoxysilane and 3-glycidoxypropyl-trimethoxysilane. Of these, 3-glycidoxypropyltrimethoxysilane is preferred. The silane coupling agent is included in the liquid hardenable resin component in an amount in the range of from 0% to about 5% by weight of the liquid hardenable resin component, preferably in an amount of about 2%.

[0017] Examples of solvents for the organic resin and silane coupling agent in the liquid hardenable resin component include, but are not limited to, methanol, butyl alcohol and N-methyl-2-pyrrolidone. Of these, methanol is preferred. The amount of the solvent utilized in the liquid hardenable resin component is in the range of from about 1% to about 10% by weight of the liquid hardenable resin component, preferably in an amount of about 5%.

[0018] Examples of hydrolyzable esters utilized in the liquid hardenable component for facilitating the coating of the resin composition on the proppant particles and for breaking gelled fracturing fluid films thereon, include, but are not limited to, a mixture of dimethylglutarate, dimethyladipate and dimethylsuccinate, sorbitol, catechol, dimethylthiolate and ter butylhydroperoxide. Of these, a mixture dimethylglutarate, dimethyladipate and dimethylsuccinate is preferred. The hydrolyzable ester is present in the liquid hardenable component in an amount in the range of from about 0.2% to about 2 percent by weight of the liquid hardenable resin component, preferably in an amount of about 1.2%.

[0019] The surfactants which can be utilized in the liquid hardenable resin component for facilitating the coating of the resin on the proppant particles, and for causing the hardenable resin to flow to the contact points between adjacent resin coated proppant particles include, but are not limited to, an ethoxylated nonyl phenol phosphate ester and mixtures of one or more cationic surface active agents and one or more non-ionic surface active agents. Such mixtures are described in U.S. Patent No. 6,311,733 issued to Todd et al. on November 6, 2001 which is incorporated herein by reference. An ethoxylated nonyl phenol phosphate ester is preferred. The surfactant or surfactants utilized are included in the liquid hardenable resin component in an amount in the range of from about 1% to about 15% by weight of the liquid hardenable resin component, preferably in an amount of about 8%.

[0020] The liquid hardening agent component is comprised of a hardening agent and a liquid carrier fluid. Examples of hardening agents that can be used include, but are not limited to, 4,4'-diaminodiphenyl sulfone, amines, amides, hexachloroacetone, 1,1,3-trichlorotrifluoroacetone, benzotrichloride, benzylchloride and benzalchloride. Of these, 4,4'-diaminodiphenyl sulfone is preferred.

5 [0021] The hardening agent is included in the liquid hardening agent component in an amount in the range of from about 20% to about 70% by weight of the liquid hardening agent component, preferably in an amount of about 45%.

[0022] The liquid carrier fluid in the liquid hardening agent component is an aqueous liquid. A preferred aqueous liquid carrier fluid is a xanthan polymer gelled aqueous liquid. The aqueous liquid is present in the liquid hardening agent component in an amount in the range of from about 30% to about 80% by weight of the liquid hardening agent component, preferably in an amount of about 55%.

10 [0023] As mentioned above, during the time that the liquid hardenable resin component and the liquid hardening agent component are continuously mixed and coated on the dry proppant particles on-the-fly, the rate of the liquid hardening agent component can be varied while the rate of the liquid hardenable resin component is held constant. Stated another way, the volume ratio of the liquid hardening agent component to the liquid hardenable resin component is varied. Preferably, the volume ratio of the liquid hardening agent component to the liquid hardenable resin component is varied from an initial volume ratio to a lower volume ratio and then back to the initial volume ratio. This procedure causes all of the proppant particles to be consolidated with the proppant particles adjacent to the well bore and the proppant particles at the front of the fracture being strongly consolidated and the proppant particles between the ends of the fracture being moderately consolidated. This arrangement effectively prevents proppant flow-back. The procedure is based on the discovery that reductions in the amount of the liquid hardening agent component from the amount that produces a very hard and strong cured resin causes the resin to become more rubbery or flexible but it still functions to consolidate the proppant particles. Thus, the middle portion of a consolidated proppant particle pack in a fracture can be resilient and have less compressive strength so long as the end portions of the pack are consolidated with high strength rigid resin.

15 [0024] A variety of fracturing fluids can be utilized in accordance with the present invention including aqueous gels, emulsions and other fluids utilized for forming fractures in subterranean zones and carrying resin composition coated proppant particles into the fractures. The aqueous gels are generally comprised of water and one or more gelling agents. The emulsions can be comprised of two immiscible liquids such as an aqueous gelled liquid and a liquefied, normally gaseous fluid, such as carbon dioxide.

20 [0025] The preferred fracturing fluids for use in accordance with this invention are aqueous gels comprised of water, a gelling agent for gelling the water and increasing its viscosity, and optionally, a cross-linking agent for cross-linking the gel and further increasing the viscosity of the fluid. The increased viscosity of the gelled or gelled and cross-linked fracturing fluid reduces fluid loss and allows the fracturing fluid to transport significant quantities of suspended resin composition coated proppant particles. The water utilized to form the fracturing fluid can be fresh water, salt water, 25 brine or any other aqueous liquid which does not adversely react with other components utilized in accordance with this invention.

30 [0026] A variety of gelling agents can be utilized including hydratable polymers which contain one or more functional groups such as hydroxyl, cis-hydroxyl, carboxyl, sulfate, sulfonate, amino or amide. Particularly useful such polymers are polysaccharides and derivatives thereof which contain one or more of the monosaccharide units galactose, mannose, glucoside, glucose, xylose, arabinose, fructose, glucuronic acid or pyranosyl sulfate. Examples of natural hydratable polymers containing the foregoing functional groups and units which are particularly useful in accordance with the present invention include guar gum and derivatives thereof such as hydroxypropyl guar and cellulose derivatives such as hydroxyethyl cellulose. Hydratable synthetic polymers and copolymers which contain the above mentioned functional groups can also be utilized. Examples of such synthetic polymers include, but are not limited to, polyacrylate, 35 polymethacrylate, polyacrylamide, polyvinyl alcohol and polyvinylpyrrolidone. The gelling agent used is generally combined with water in an amount in the range of from about 0.1% to about 1% by weight of the water.

40 [0027] Examples of cross-linking agents which can be utilized to further increase the viscosity of a gelled fracturing fluid are alkali metal borates, borax, boric acid and compounds which are capable of releasing multivalent metal ions in aqueous solutions. Examples of the multivalent metal ions are chromium, zirconium, antimony, titanium, iron, zinc or aluminum. When used, the cross-linking agent is generally added to the gelled water in an amount in the range of from about 0.01% to about 1% by weight of the water.

45 [0028] The above described gelled or gelled and cross-linked fracturing fluids typically also include internal delayed gel breakers such as those of the enzyme type, the oxidizing type, the acid buffer type and the temperature activated type, all of which are well known to those skilled in the art. The gel breakers cause the viscous carrier fluids to revert to thin fluids that can be produced back to the surface after they have been used to place proppant particles in subterranean fractures. The fracturing fluids can also include one or more of a variety of well known additives such as gel stabilizers, fluid loss control additives, clay stabilizers, bacteriacides and the like.

50 [0029] The proppant particles utilized in accordance with the present invention are generally of a size such that

formation particulate solids which migrate with produced fluids are prevented from being produced from the subterranean zone. Various kinds of proppant can be utilized including graded sand, bauxite, ceramic materials, glass materials and the like. Generally, the proppant particles have a size in the range of from about 2 to about 400 mesh, U.S. Sieve Series. The preferred proppant is graded sand having a particle size in the range of from about 10 to about 70 mesh, U.S. Sieve Series. Preferred sand particle size distribution ranges are one or more of 10-20 mesh, 20-40 mesh, 40-60 mesh or 50-70 mesh, depending on the particular size and distribution of formation solids to be screened out by the consolidated proppant particles.

**[0030]** A preferred improved method of this invention for coating dry proppant particles with a hardenable resin composition and suspending the coated proppant particles in a fracturing fluid, the resin composition hardening and consolidating the resin coated proppant particles into a high strength permeable mass which prevents proppant flow-back after being placed in one or more fractures in a subterranean zone comprising the steps of: (a) providing a liquid hardenable resin component comprised of a hardenable resin, a silane coupling agent, a solvent for the resin, one or more hydrolyzable esters for breaking gelled fracturing fluid films on the proppant particles, and a surfactant for facilitating the coating of the resin on the proppant particles and for causing the hardenable resin to flow to the contact points between adjacent resin coated proppant particles; (b) providing a liquid hardening agent component comprised of a hardening agent suspended or dissolved in a liquid carrier fluid; (c) providing a source of dry proppant particles; (d) providing a gelled liquid fracturing fluid; (e) pumping the gelled liquid fracturing fluid into the subterranean zone to form the one or more fractures therein and to place the hardenable resin composition coated proppant particles in the fractures; (f) as the fractures are formed in step (e), continuously mixing the liquid hardenable resin component with the liquid hardening agent component on-the-fly to form the hardenable resin composition; (g) continuously coating the hardenable resin composition produced in step (f) onto dry proppant particles conveyed from the source thereof on-the-fly to form resin composition coated proppant particles; (h) continuously mixing the resin composition coated proppant particles produced in step (g) with the fracturing fluid pumped in accordance with step (e) on-the-fly whereby the resin composition coated proppant particles are suspended therein; (i) terminating steps (e), (f), (g) and (h) when the resin composition coated proppant particles have been placed in the one or more fractures; and (j) allowing the hardenable resin composition on the resin composition coated proppant particles to harden and consolidate the proppant particles into one or more high strength permeable packs which prevent proppant flow-back.

**[0031]** Another preferred improved method of coating dry proppant particles with a hardenable resin composition and suspending the coated proppant particles in a fracturing fluid, the resin composition hardening and consolidating the resin coated proppant particles into a high strength permeable mass which prevents proppant flow-back after being placed in one or more fractures formed in a subterranean zone comprising the steps of: (a) providing a liquid hardenable resin component comprised of a hardenable resin, a silane coupling agent, a solvent for the resin, one or more hydrolyzable esters for breaking gelled fracturing fluid films on the proppant particles, and a surfactant for facilitating the coating of the resin on the proppant particles and for causing the hardenable resin to flow to the contact points between adjacent resin coated proppant particles; (b) providing a liquid hardening agent component comprised of a hardening agent suspended or dissolved in a liquid carrier fluid; (c) providing a source of dry proppant particles; (d) providing a gelled liquid fracturing fluid; (e) pumping the gelled liquid fracturing fluid into the subterranean zone to form the one or more fractures therein and to place the resin composition coated proppant particles in the fractures; (f) as the fractures are formed in step (e), continuously mixing the liquid hardenable resin component with the liquid hardening agent component on-the-fly to form the hardenable resin composition; (g) varying the volume ratio of the liquid hardening agent component to the liquid hardenable resin component during step (f); (h) continuously coating the hardenable resin composition produced in steps (f) and (g) onto dry proppant particles conveyed from the source thereof on-the-fly to form resin composition coated proppant particles; (i) continuously mixing the resin composition coated proppant particles produced in step (h) with the fracturing fluid pumped in accordance with step (e) on-the-fly whereby the resin composition coated proppant particles are suspended therein; (j) terminating steps (e), (f), (g), (h) and (i) when the resin composition coated proppant particles have been placed in the one or more fractures; and (k) allowing the hardenable resin composition on the resin composition coated proppant particles to harden and consolidate the proppant particles into one or more high strength permeable packs which prevent proppant flow-back.

**[0032]** In order to further illustrate the methods of the present invention, the following examples are given.

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### Example 1

**[0033]** To determine the effect of resin concentration on the consolidation strengths of proppant packs, bauxite proppant was dry coated with various amounts of mixed resin compositions. The concentration is expressed in terms of weight percent of proppant. After dry coating with the mixed resin, the proppant was mixed with a cross-linked 30 pound per 1,000 gallon linear carboxymethyl guar fracturing fluid, poured into a consistometer, stirred for 60 minutes at 175°F to simulate pumping, transferred to flow cells, packed, and cured in an oven at 300°F for 3 hours with and without 500-psi closure stress. A consistometer is a device designed to stir a solid containing slurry at a desired temperature.

After curing, the flow cells were removed from the oven and allowed to cool to less than 100°F. The flow cells were then connected to a tap water faucet for flow back tests to determine how much proppant would be released from the cured pack and flow-back with the water. The water flow rate was steadily increased from 0 to more than 10 liters/minute (i.e., the maximum flow rate of the faucet). The flow cell had a 0.5-inch diameter perforation. After the flow-back testing, the consolidated proppant cores were removed from the flow cells and prepared for unconfined compressive strength measurements (Table I).

TABLE I

Effect Of Resin Concentration On Consolidation And Flow-Back			
Resin Concentration on Proppant, % by Weight of Resin Coated Proppant	Unconfined Compressive Strength Without Closure Pressure, psi	Unconfined Compressive Strength With Closure Pressure, psi	Proppant Flow-Back Amount, grams
1	51	150	None
2	1088	1194	None
3	1474	1585	None
3 (Repeat)	1536	1786	None

### Example 2

[0034] To determine the effect of cure time on the consolidation strength of proppant packs, bauxite proppant was dry coated with a resin composition using a concentration of 2% by weight of proppant. After dry coating with the resin, the proppant was mixed with a cross-linked 30 pound per gallon linear carboxymethyl guar fracturing fluid, poured into the consistometer, stirred for 60 minutes at 175°F to simulate pumping, transferred to flow cells, packed, and cured in oven at 300°F for 1, 2, 4 and 16 hours without closure stress. After curing, the proppant packed cores were obtained from the flow cells for unconfined compressive strength measurements (Table II).

TABLE II

Effect Of Cure Time On Consolidation	
Cure Time, Hrs	Unconfirmed Compressive Strength, psi
1	245
2	980
4	1230
16	1200

### Example 3

[0035] To determine the effect of simulated pump time on the consolidation strength, bauxite proppant was dry coated with a resin composition at a concentration of 3% by weight of proppant. After dry coating with the resin, the proppant was mixed with a cross-linked 30 pound per 1,000 gallon linear carboxymethyl guar fracturing fluid which was poured into a consistometer. Various stir periods were used at 175°F to simulate pumping after which portions of the fracturing fluid were transferred to flow cells, packed, and cured in an oven at 300°F for 3 hours with and without 500-psi closure stress. After curing, the cured proppant pack cores were removed from the flow cells for unconfined compressive strength measurements (Table III).

TABLE III

Effect Of Simulated Pump Time On Consolidation			
Test No.	Description Of Test	Unconfined Compressive Strength Without Closure Pressure, psi	Unconfined Compressive Strength With Closure Pressure, psi
1	Stirred in consistometer for 30 min. at 175°F. Stopped stirring and remained at 175°F for 3 hours. Packed cross-linked slurry into flow cells and cured at 300°F for 3 hours without closure applied. Stirred in consistometer for 30 min. at 175°F.	1410	
2	Packed in flow cell without closure, remained in heat bath at 175°F for 3 hours. Applied 500 psi closure, cured at 300°F for 3 hours.		1945
3	Stirred in consistometer for 1 hour at 175°F. Packed and cured at 300°F for 3 hours.	1560	1690
4	Stirred in consistometer for 1 hour at 175°F. Packed and cured at 300°F for 3 hours.	1790	1930
5	Stirred in consistometer for 1 hour at 175°F. Packed and cured at 300°F for 3 hours.	1680	1795

**Example 4**

[0036] The procedure of Example 2 was repeated except that portions of the proppant were dry coated with resin compositions containing varying amounts of hardening agent. Each of the resin coated proppant portions were mixed with portions of a cross-linked 30 pound per gallon linear carboxymethyl guar fracturing fluid and tested as indicated in Example 2.

TABLE IV

Effect Of Varying Amounts Of Liquid Hardening Agent Component On Consolidation and Flow-Back				
Test No.	Volume % Liquid Hardening Agent Component	Cure Time, hrs	Unconfined Compressive Strength, psi	Proppant Flow-Back Amount, grams
1	0	3	6	None
2	0	20	7	None
3	5	3	9	None
4	5	20	22	None
5	10	3	140	None
6	10	20	150	None
7	25	3	425	None
8	50	3	1155	None
9	100	3	1680	None

[0037] As indicated in Table IV, various amounts of liquid hardening agent component ranging from 0 to 100 percent of the initial amount can be mixed with the liquid hardenable resin component to achieve different degrees of rubbery/

flexibility and consolidation strengths for the proppant packs. A proppant pack can be transformed into a complete consolidated pack by increasing the amount of liquid hardening agent component above 25 percent, depending on the desired level of consolidation strength and cure time. The consolidation was obtained without any closure stress applied. The flow-back testing was also performed using a flow cell that had a 0.5-inch diameter perforation. Despite of 5 low consolidation strengths, the proppant packs were flexible, yet coherent permeable masses allowing the proppant core samples to withstand high water flow rates simulating high production flow rate wells without producing any proppant from the flow cell (Table IV).

10 **Claims**

1. A method of providing resin-coated proppant particles in a fracture in a subterranean zone, which method comprises
  - 15 (a) pumping gelled liquid fracturing fluid into said subterranean zone to form one or more fractures therein, and;
  - (b) as said fractures are formed in step (a), continuously mixing a liquid hardenable resin component with a liquid hardening agent component on-the-fly to form a hardenable resin composition; said liquid hardenable resin component being comprised of a hardenable resin, a silane coupling agent, a solvent for said resin, one or more hydrolysable esters for breaking gelled fracturing fluid films on proppant particles, and a surfactant for facilitating the coating of resin on said proppant particles and for causing said hardenable resin to flow to the contact points between adjacent resin coated proppant particles; and said liquid hardening agent component being comprised of a hardening agent suspended or dissolved in a liquid carrier fluid;
  - 20 (c) continuously coating said hardenable resin composition produced in step (b) onto dry proppant particles on-the-fly to form resin composition coated proppant particles;
  - (d) continuously mixing said resin composition coated proppant particles produced in step (c) with said fracturing fluid pumped in accordance with step (a) on-the-fly whereby said resin composition coated proppant particles are suspended therein;
  - 25 (e) terminating steps (a), (b), (c) and (d) when said resin composition coated proppant particles have been placed in said one or more fractures; and
  - (f) allowing said hardenable resin composition on said resin composition coated proppant particles to harden and consolidate said proppant particles into one or more high strength permeable packs which prevent proppant particle flow-back.
2. A method according to claim 1, wherein said hardenable resin in said liquid hardenable resin component is an 35 organic resin selected from bisphenol A-epichlorohydrin resin, polyepoxide resin, novolak resin, polyester resin, phenol-aldehyde resin, urea-aldehyde resin, furan resin, urethane resin and any mixture of two or more thereof.
3. A method according to claim 1 or 2, wherein said silane coupling agent is N-2-(aminoethyl)-3-aminopropyltrimethoxysilane or 3-glycidoxypropyltrimethoxysilane.
- 40 4. A method according to claim 1, 2 or 3, wherein said solvent for said resin in said liquid hardenable resin component is methanol, butyl alcohol or N-methyl-2-pyrrolidone.
5. A method according to claim 1, 2, 3 or 4, wherein said one or more hydrolyzable esters is a mixture of dimethylglutarate, dimethyladipate and dimethylsuccinate, or sorbitol, or catechol, or dimethylthiolate or terbutylhydroperoxide.
- 45 6. A method according to any of claims 1 to 5, wherein said surfactant is an ethoxylated nonyl phenol phosphate ester or a mixture of one or more cationic surface active agents and one or more non-ionic surface active agents.
7. A method according to any of claims 1 to 6, wherein said hardening agent in said liquid hardening agent component is 4,4'-diaminodiphenyl sulfone, amines, amides, hexachloroacetone, 1,1,3-trichlorotrifluoro-acetone, benzotrichloride, benzylchloride and benzalchloride.
- 50 8. A method according to any of claims 1 to 7, wherein said liquid carrier fluid in said liquid hardening agent component is an aqueous liquid, preferably a xanthan polymer gelled aqueous liquid.
9. A method according to any of claims 1 to 8, which further comprises the step of varying the volume ratio of said

liquid hardening agent component to said liquid hardenable resin component during the time steps (a) to (d) are carried out.

5 10. A method according to claim 9, wherein the volume ratio of said liquid hardening agent component to said liquid hardenable resin component is varied from an initial volume ratio, preferably of from 1:100 to 1:2, to a lower volume ratio, preferably up to 1:5, and then back to said initial volume ratio.

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## EUROPEAN SEARCH REPORT

Application Number  
EP 03 25 0030

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The present search report has been drawn up for all claims			
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THE HAGUE		17 April 2003	Boulon, A
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			
T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

**ANNEX TO THE EUROPEAN SEARCH REPORT  
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